COMBINING THE POWER OF IRMPD WITH ION-MOLECULE REACTIONS: THE STRUCTURE AND REACTIVITY OF RADICAL IONS OF CYSTEINE AND ITS DERIVATIVES

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Most of the work on peptide radical cations has involved protons as the source of charge. Nonetheless, using metal ions as charge sources often offers advantages like stabilization of the structure via multidentate coordination and the elimination of the "mobile proton". Moreover, characterization of metal-bound amino acids is of general interest as the interaction of peptide side chains with metal ions in biological systems is known to occur extensively. In the current study, we generate thiyl radicals of cysteine and homocysteine in the gas phase complexed to alkali metal ions. Subsequently, we utilize infrared multiple-photon dissociation (IRMPD) and ion-molecule reactions (IMR) to characterize the structure and reactivity of these radical ions.

Our group has worked extensively with the cysteine-based radical cations and anions, characterizing the gas-phase reactivity and rearrangement of the amino acid and several of its derivatives. In a continuation of this work, we are perusing the effects of metal ions as the charge bearing species on the reactivity of the sulfur radical. Our S-nitroso chemistry can easily be used in conjunction with metal ion coordination to produce initial S-based radicals in peptide radical-metal ion complexes. In all cases we have been able to achieve radical formation with significant yield to study reactivity. Ion-molecule reactions of metallated radicals with allyl iodide, dimethyl disulfide, and allyl bromide have all shown decreasing reactivity going down group 1A.

Recently, we determined the experimental IR spectra for the homocysteine radical cation with Li+, Na+, and K+ as the charge bearing species at the FELIX facility. For comparison, the protonated IR spectrum of homocysteine has previously been obtained by our group. A preliminary match of the IR spectra has been confirmed. Finally, calculations are underway to determine the bond distances of all the metal adduct structures.